# Platinum nanoparticle immobilization onto carbon nanotubes using Ptsputtered room-temperature ionic liquid

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### **Experimental Details**

Preparation of RTILs:	<i>N</i> , <i>N</i> , <i>N</i> -trimethyl- <i>N</i> -propylammonium	bis(trifluoromethanesulfonyl)amide			
$([Me_3PrN][Tf_2N]),$	N,N,N-triethyl-N-octylammonium	bis(trifluoromethanesulfonyl)amide			
$([Et_3OctN][Tf_2N]),$	N-methyl-N-propylpyridinium	bis(trifluoromethanesulfonyl)amide			
([MePrPyr][Tf <sub>2</sub> N]),	N-butyl-N-methylpyridinium	bis(trifluoromethanesulfonyl)amide			
([MeBuPyr][Tf <sub>2</sub> N]),	1-ethyl-3methylimidazolium	bis(trifluoromethanesulfonyl)amide			
([EtMeIm][Tf <sub>2</sub> N]),	1-allyl-3-ethylimidazolium	bis(trifluoromethanesulfonyl)amide			
([AllyEtIm][Tf <sub>2</sub> N]) wer	re purchased from Kanto Chem	ical Co., Inc. N-methyl-N-			
methoxymethylpyridiniun	n bis(trifluoromethanesulfonyl)amide	([Me(MeOMe)Pyr][Tf <sub>2</sub> N]) was			
provided by Otsuka Chemical Co., Ltd. These RTILs were purified with the method described in					
previous reports before use. <sup>1-3</sup>					

N,N,N-tributyl-N-methylammonium bis(trifluoromethanesulfonyl)amide ([Bu<sub>3</sub>MeN][Tf<sub>2</sub>N]) and 1-hexyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide ([HexMeMeIm][Tf<sub>2</sub>N]) were prepared by mixing exactly equal molar amounts of the purified organic chloride salts, N,N,Ntributyl-N-methylammonium chloride and 1-hexyl-2,3-dimethylimidazolium chloride, and Li[Tf<sub>2</sub>N] in ultrapure water with dichloromethane. The solution was agitated at room temperature for 12 hrs. The dichloromethane phase containing RTIL was washed repeatedly with reverse osmosis (RO) water until the water phase was found to contain no chloride as determined by the addition of a few drops of a silver nitrate solution.<sup>3</sup> Chemical structures of all RTILs used in this study are depicted in Figure S1.

*Preparation of Pt nanoparticle*: The RTILs were dried in vacuum prior to use. A soda glass plate  $(2.5 \times 2.5 \text{ cm})$ , on which RTIL (0.4 mL) was spread, was set in a Cressington108 auto SE sputter coater. A Pt foil target (ø5.7 cm, 99.98 %) was placed on 4.5 cm above the glass plate. Sputter deposition onto RTIL for Pt nanoparticle preparation was conducted with sputter current of 40 mA in

dry Ar (99.999 %) atmosphere whose pressure did not exceed  $7 \pm 1$  Pa. The sputtering was conducted by direct current (DC) mode at room temperature (298 ± 2 K).

*Characterization of Pt nanoparticle and Pt–SWCNT composite*: Morphology of the obtained Pt nanoparticle and Pt nanoparticle-immobilized SWCNT (Pt–SWCNT) composite material was observed by a HITACHI H-7650 transmission electron microscope (TEM) with an acceleration voltage of 100 kV. Before the TEM observation, the sample grids were prepared by dropping the Pt sputtered-RTIL and the Pt–SWCNT dispersed isopropanol solution onto a TEM grid (ø3.0 mm, copper, 400 mesh) and a TEM microgrid (ø3.0 mm, copper, 167 mesh), respectively. The original TEM grids were coated with an amorphous carbon thin layer. Elemental analysis of the specimens was performed with an EDAX Genesis-XM2 energy dispersive X-ray spectrometer (EDX) mounted on the TEM. The Pt content in the Pt–SWCNT was measured by a Shimadzu ICPS-7510 inductively coupled plasma atomic emission spectrometer (ICP-AES). The chemical state of the elements contained in the Pt–SWCNT was examined by a KRATOS AXIS-ULYRA HSA X-ray photoelectron spectroscopy.

*Electrochemical experiments*: Electrocatalytic activities for a Pt nanoparticle–SWCNT (Pt–SWCNT) composite material prepared in this investigation toward oxygen reduction were examined with a Hokuto Denko HZ-5000 potentiostat/galvanostat controlled with a desktop computer. The electrochemical experiments were conducted by using a three-electrode cell. A glassy carbon (GC) rotating ring-disk electrode (RRDE) (Pt ring: 0.1866 cm<sup>2</sup>; GC disk: 0.2475 cm<sup>2</sup> (Pine Instruments)) was used as the working electrode. After preparation of Pt-SWCNT (1 mg) dispersed in *i*-propanol solution (0.2 mL), the solution of 5  $\mu$ L was applied to the GC disk of the RRDE, and the *i*-propanolic solution was evaporated in air. Finally the GC disk was covered with a Nafion<sup>®</sup> *i*-propanolic solution of 5  $\mu$ L to robustly fix the Pt–SWCNT on the GC. A Pt mesh was used as the counter

electrode. The Ag/AgCl double-junction electrode immersed in a KCl-saturated solution was employed as the reference electrode. All potential values are reported with respect to normal hydrogen electrode (NHE). The prepared Pt–SWCNT working electrode was pretreated with multiple potential scans between 0 and +1.2 V (*vs.* NHE) in 0.1 M HClO<sub>4</sub> aqueous solution under dry N<sub>2</sub> condition before oxygen reduction experiments. Cyclic voltammograms were recorded at the Pt–SWCNT modified RRDE electrode in 0.1 M HClO<sub>4</sub> aqueous solution saturated with N<sub>2</sub> or O<sub>2</sub> gas. Prior to the measurements, the solution was aerated with N<sub>2</sub> or O<sub>2</sub> more than 30 min. Hydrodynamic voltammetry was carried out under O<sub>2</sub> atmosphere. The scan rate was 10 mV s<sup>-1</sup> and the rotating rate was 1200 rpm. The potential at the ring was maintained at 1.20 V (*vs.* NHE) so as to entirely oxidize hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) generated by an undesirable two-electron O<sub>2</sub> reduction reaction. H<sub>2</sub>O<sub>2</sub> generation rate, *x*<sub>H2O2</sub> (%), on the GC disk was calculated from the following formula<sup>4</sup>

$$x_{\rm H_2O_2} = \frac{200I_{\rm R}/N}{I_{\rm D} + I_{\rm R}/N}$$

where  $I_{\rm R}$  is the ring current,  $I_{\rm D}$  is the disk current and *N* is the collection efficiency, here, the *N* value was 0.40. By this electrochemical analysis, we can estimate the percentage for the two-electron reaction involved in the electrochemical O<sub>2</sub> reduction reaction at each potential as  $x_{\rm H2O2}$ .

## **Additional Results and Discussion**

*Electrochemical oxygen reduction experiments*: Metal nanoparticle–CNT composite material is expected to be a next-generation electrode catalyst for polymer electrolyte fuel cell (PEFC). There are many papers on electrocatalytic characteristics of metal nanoparticle–SWCNT composite.<sup>5</sup> We examined electrocatalytic activity of the Pt–SWCNT prepared by the method depicted in Scheme S1 to oxygen reduction reaction (ORR). The Pt–SWCNT modified GC disk (Pt–SWCNT/GC) electrode was prepared by the method described in Experimental Details. The prepared Pt–SWCNT working electrode was pretreated with multiple potential scans between 0 and +1.2 V (vs. NHE) in 0.1 M

HClO<sub>4</sub> aqueous solution under dry N<sub>2</sub> condition before the electrochemical experiments. Fig. S6 shows cyclic voltammograms recorded at the Pt-SWCNT/GC electrode in 0.1 M HClO<sub>4</sub> aqueous solution saturated with N2 or O2 gas. Under N2 atmosphere, several characteristic waves appeared at 0.60 to 1.20 V (vs. NHE) and 0.05 to 0.30 V. The former is attributable to oxidation/reduction of Pt atoms on the surface of Pt nanoparticle, and the latter is due to adsorption/desorption of hydrogen atoms onto the Pt nanoparticle. When the voltammetry was conducted in the O<sub>2</sub> atmosphere, a distinctive O<sub>2</sub> reduction wave appeared at negative potential than ca. 0.90 V. Further investigation was carried out by means of hydrodynamic voltammetry using a rotating ring-disk electrode in order to elucidate whether the O<sub>2</sub> reduction proceeds by a useful four-electron reduction process. From the voltammograms shown in Fig. S7, we can determine the reaction precisely by an appropriate electroanalytical chemistry technique.<sup>6</sup> Fig. S8 presents a generation rate of H<sub>2</sub>O<sub>2</sub> that was yielded by a two-electron ORR.<sup>4</sup> Lower H<sub>2</sub>O<sub>2</sub> generation rate means that the ORR predominantly proceeds via a four-electron O<sub>2</sub> reduction reaction. The estimated H<sub>2</sub>O<sub>2</sub> generation rate was close to 0 % at ca. 0.68 to 0.90 V. At potentials where O<sub>2</sub> reduction current was reached to the diffusion-limited current, H<sub>2</sub>O<sub>2</sub> production was recognized, but the H<sub>2</sub>O<sub>2</sub> generation rate maintained low values that were below 7% even at 0.10 V. This result shows that the Pt-SWCNT has a favorable electrocatalytic activity for ORR.

#### References

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0, N 0 F<sub>3</sub>C 0, CF<sub>3</sub>

*N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide ([Me<sub>3</sub>PrN][Tf<sub>2</sub>N])

N,N,N-triethyl-N-pentylammonium bis(trifluoromethanesulfonyl)amide ([Et<sub>3</sub>PeN][Tf<sub>2</sub>N])

0 F<sub>3</sub>C S O O C F<sub>3</sub>C C F<sub>3</sub>C

N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([MePrPyr][Tf<sub>2</sub>N])

F<sub>3</sub>C

1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([EtMelm][Tf<sub>2</sub>N])

F<sub>3</sub>C<sup>N</sup>S<sup>C</sup>CF<sub>3</sub> N-butyl-N-methylpyrrolidinium

bis(trifluoromethanesulfonyl)amide ([BuMePyr][Tf<sub>2</sub>N])

F<sub>3</sub>C

1-allyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide ([AllyEtIm][Tf<sub>2</sub>N])

Fig. S1 Chemical structure of RTILs used in this study.

C<sub>4</sub>H<sub>9</sub>

N,N,N-tributyl-N-methylammonium bis(trifluoromethanesulfonyl)amide ([Bu<sub>3</sub>MeN][Tf<sub>2</sub>N])

S\_N\_0 S\_O\_0 CF3 F<sub>3</sub>C

N-methoxymethyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([(MeOMe)MePyr][Tf<sub>2</sub>N])

F<sub>3</sub>C

1-hexyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide ([HexMeMelm][Tf<sub>2</sub>N])



**Fig. S2** (a) TEM image and (b) size distribution diagram of Pt nanoparticles prepared in N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide ([Me<sub>3</sub>PrN][Tf<sub>2</sub>N]) by RTIL-sputtering method.



**Fig. S3** (a) EDX spectra of Pt–SWCNT composite prepared by using Pt-sputtered [Me<sub>3</sub>PrN][Tf<sub>2</sub>N]. The Cu intensity is derived from a Cu grid used for TEM observation. (b-d) Size distribution diagrams of Pt nanoparticles on Pt–SWCNT composite. The Pt-sputtered RTIL was  $[Me_3PrN][Tf_2N]$ . The sputtering time was (b) 300 sec, (c) 600 sec, and (d) 900 sec.



**Fig. S4** TEM images of Pt–SWCNT composite prepared by using various RTILs. The RTILs were (a)  $[Et_3PeN][Tf_2N]$ , (b)  $[Bu_3MeN][Tf_2N]$ , (c)  $[MePrPyr][Tf_2N]$ , (d)  $[BuMePyr][Tf_2N]$ , (e)  $[(MeOMe)MePyr][Tf_2N]$ , (f)  $[AllyEtIm][Tf_2N]$ , and (g)  $[HexMeMeIm][Tf_2N]$ .



**Fig. S5** Size distribution diagrams of Pt nanoparticles on Pt–SWCNT composite prepared by using various Pt-sputtered RTILs. The RTILs were (a)  $[Et_3PeN][Tf_2N]$ , (b)  $[Bu_3MeN][Tf_2N]$ , (c)  $[MePrPyr][Tf_2N]$ , (d)  $[BuMePyr][Tf_2N]$ , (e)  $[(MeOMe)MePyr][Tf_2N]$ , (f)  $[AllyEtIm][Tf_2N]$ , and (g)  $[HexMeMeIm][Tf_2N]$ .



**Fig. S6** Cyclic voltammograms recorded at a Pt–SWCNT modified GC electrode in 0.1 M HClO<sub>4</sub> aqueous solution under (•••) N<sub>2</sub> and (—) O<sub>2</sub> atmosphere. The RTIL used for the Pt nanoparticle preparation was [Me<sub>3</sub>PrN][Tf<sub>2</sub>N]. The scan rate was 10 mV sec<sup>-1</sup>.

![](_page_12_Figure_1.jpeg)

**Fig. S7** Hydrodynamic voltammograms for ORR recorded at a Pt–SWCNT modified rotating ringdisk electrode in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> aqueous solution at 298 K. The electrodes were (top) Pt ring and (bottom) Pt–SWCNT modified GC disk. The RTIL used for Pt nanoparticle preparation was [Me<sub>3</sub>PrN][Tf<sub>2</sub>N]. The potential for the ring electrode was 1.20 V. The scan rate was 10 mV s<sup>-1</sup>. The rotation rate was 1200 rpm.

![](_page_13_Figure_1.jpeg)

**Fig. S8** Hydrogen peroxide generation rate determined by hydrodynamic voltammetric method at different applied potentials. The data was constructed from Fig. S7.

![](_page_14_Figure_1.jpeg)

Scheme S1 Fabrication method for Pt nanoparticle-immobilized SWCNT composite material used in this investigation.

**Table S1** Summary of Pt nanoparticle prepared in [Me<sub>3</sub>PrN][Tf<sub>2</sub>N] by RTIL–magnetron sputtering method and the Pt–SWCNT fabricated from the Pt-dispersed RTILs

Sputtering time (sec)	Mean particle size in sputtered RTIL $(nm)^a$	Pt concentration in sputtered RTIL $(\text{mmol } \text{L}^{-1})^b$	Mean particle size on SWCNT (nm) <sup><i>a</i></sup>	Pt loading amount on Pt–SWCNT (wt %) <sup>b</sup>
300	2.3	8.2	3.5	11.8
600	2.3	16.3	3.2	28.4
900	2.4	21.6	3.5	32.0

<sup>*a*</sup> Estimated by TEM observation. <sup>*b*</sup> Calculated from ICP-AES measurement.

RTILs	Mean particle size in sputtered RTIL (nm) <sup>b</sup>	Mean particle size on SWCNT $(nm)^b$	Pt loading amount on SWCNT $(wt\%)^c$
[Me <sub>3</sub> PrN][Tf <sub>2</sub> N]	2.4	3.5	32.0
[Et <sub>3</sub> PeN][Tf <sub>2</sub> N]	1.4	2.6	23.6
[Bu <sub>3</sub> MeN][Tf <sub>2</sub> N]	1.7	3.1	21.1
[MePrPyr][Tf <sub>2</sub> N]	1.7	3.4	29.7
[BuMePyr][Tf <sub>2</sub> N]	1.4	3.0	16.0
[(MeOMe)MePyr][Tf <sub>2</sub> N]	1.6	2.8	17.7
[EtMeIm][Tf <sub>2</sub> N]	_d	_d	1.30
[AllyEtIm][Tf <sub>2</sub> N]	1.8	2.3	2.89
[HexMeMeIm][Tf <sub>2</sub> N]	1.9	3.1	5.01

**Table S2** Mean particle size of the Pt nanoparticles and the Pt loading amount on SWCNT<sup>a</sup>

<sup>*a*</sup> Sputtering time was 900 sec. <sup>*b*</sup> Estimated by TEM observation. <sup>*c*</sup> Calculated from ICP-AES measurement. <sup>*d*</sup> We could not estimate these values precisely, because they were very fine particles not exceeding 1.00 nm in diameter.